Part I

Concepts

In this first part of the book, the basic concepts and tools are presented for the description of quasicrystals and their structurally closely related periodic approximants. We will use both d-dimensional (dD) and n-dimensional (nD) approaches, where d is the dimension of the physical space and n that of the higher-dimensional embedding space ($n > d$).

In dD physical space, quasiperiodic structures can be described based on tilings or coverings. By tiling we mean a gapless packing of non-overlapping copies of a finite number of unit tiles. In analogy to a crystallographic lattice, such a tiling may be seen as a *quasilattice* with more than one unit cell of general shape. In a covering, one or more types of partially overlapping *covering clusters* fully cover a tiling or quasiperiodic pattern. In the nD description, dD quasiperiodic structures result from irrational physical-space cuts of appropriate periodic nD hypercrystal structures. Rational approximants can be obtained in the same way after shearing hypercrystal structures into the respective rational cut orientations.

In the nD approach, otherwise hidden structural correlations are revealed. For instance, the formation of diffraction patterns with Bragg reflections *and* 5-fold symmetry, causing so much controversy in the first time after the discovery of quasicrystals,[1] can be easily explained in this way. The nD approach also clearly identifies a particular kind of correlated atomic jumps (phason flips) as originating from phason modes, which are excitations already known from the study of incommensurately modulated structures. Despite the power and elegance of the nD approach, one has to keep in mind, however, that real quasicrystals are 3D objects and that their physical interactions take place in three dimensions, indeed.

What is a Crystal?

Before we define the term *quasicrystal* we should clarify what we mean by *crystal* and nD *(hyper)crystal*, in general. In the *International Tables for Crystallography, Vol A, chapter 8.1 Basic concepts*,[2] one will find the following:

> Crystals are finite real objects in physical space which may be idealized by infinite three-dimensional periodic crystal structures in point space. Three-dimensional periodicity means that there are translations among the symmetry operations of the object with the translation vectors spanning a three-dimensional space. Extending this concept of crystal structure to more general periodic objects and to n-dimensional space, one obtains the following definition:

[1] see, e.g., W. Steurer, S. Deloudi (2008): Fascinating Quasicrystals. Acta Crystallogr. A **64**, 1–11, and references therein.

[2] H. Wondratschek: Basic Concepts. In: International Tables for Crystallography, vol. A, Kluwer Academic Publisher, Dordrecht/Boston/London, pp. 720–740 (2002)

Definition: An object in n-dimensional point space E^n is called an n-dimensional crystallographic pattern or, for short, crystal pattern if among its symmetry operations

(i) there are n translations, the translation vectors $\mathbf{t}_1, \ldots, \mathbf{t}_n$ of which are linearly independent,

(ii) all translation vectors, except the zero vector $\mathbf{o}$, have a length of at least $d > 0$.

Condition (i) guarantees the n-dimensional periodicity and thus excludes subperiodic symmetries like layer groups, rod groups and frieze groups. Condition (ii) takes into account the finite size of atoms in actual crystals.

A crucial property of ideal, fully ordered crystals of any dimension is that they possess pure point Fourier spectra. This means that their diffraction patterns show Bragg reflections (Dirac δ-peaks) only, and no structural diffuse scattering. A real crystal can be described by comparing it with the model of an ideal crystal and by classifying the deviations from it. In the following, some terms are listed which are used for the description of real crystals or their idealized models:

Ideal crystal The counterpart to a real crystal. Infinite mathematical object with an idealized crystal structure; an ideal crystal can be ordered or disordered (disordered ideal crystal); if it is disordered, it is not periodic anymore, however, it has a periodic average structure.

Real crystal The counterpart to an ideal crystal. Really existing crystal which can be perfect or imperfect.

Perfect crystal Crystal in thermodynamic equilibrium, which can be ordered or disordered; the only defects possible are point defects such as thermal vacancies, impurities.

Imperfect crystal Crystal containing additionally defects that are not in thermodynamic equilibrium such as dislocations.

Nanocrystal Real crystal with dimensions on the scale of nanometers; due to the large surface area, its structure may fundamentally differ from that of larger crystals with the same composition and thermal history.

Metacrystal Crystal consisting of building units other than atoms (ions, molecules), such as photonic or phononic crystals.

What is a Quasicrystal?

One of the terms missing in the above list is *aperiodic crystal* which is used as hypernym for incommensurately modulated structures (IMS), composite crystals (CS), and quasicrystals QC. Although their structures lack dD translational periodicity, their Fourier spectra show Bragg peaks only. This property has been used by the *IUCr Ad-interim Commission on Aperiodic Crystals* to identify aperiodic crystals by their *essentially discrete diffraction diagram*.[3]

[3] *Ad interim Commission on Aperiodic Crystals*. Acta Crystallogr. A **48**, 928 (1992)

Consequently, dD translational periodicity is no more seen as a necessary condition for crystallinity. The reciprocal space definition of a crystal by its spectral properties can be much simpler than the one based on direct space. Additionally, it has the advantage of being directly accessible experimentally by diffraction methods.

However pragmatic this definition may be, it is also fuzzy. The term diffraction diagram refers to an experimentally obtained image, but does not take into account that the shapes of reflections depend on the kind of radiation used, the resolution and dynamic range of the detector as well as the quality and size of the crystal studied. A strongly absorbing, large, and irregularly shaped crystal of poor quality, for instance, would not at all give an essentially discrete diffraction diagram even for simple periodic structures.

Consequently, the concept of an aperiodic crystal has to refer to an ideal aperiodic crystal of infinite size and to its Fourier spectrum rather than to its diffraction image. A definition of the different types of aperiodic crystals in general and of quasicrystals in particular will be given in chapter 3.

How do we use the term *quasicrystal* in this book? By the term *quasicrystal* we denote real crystals with diffraction patterns showing *non-crystallographic symmetry*. This experiment-related reciprocal space definition of quasicrystals makes symmetry analysis simple and allows the application of tools that are well established in standard crystal structure analysis.

We clearly want to distinguish between quasicrystals (QC) in this meaning and the other kinds of aperiodic crystals with *crystallographic symmetry* such as incommensurately modulated structures (IMS) and composite structures (CS). In the mathematical meaning of the term quasiperiodicity, all three of them are quasiperiodic structures, which have some similarities in their higher-dimensional description. The main difference between a QC and an IMS is that an IMS can be described as modulation of a periodic crystal structure. If the modulation amplitude approaches zero, the periodic basic structure of the IMS is obtained. A CS, on the other hand, can be described as, sometimes mutually modulated, intergrowth of periodic structures. Such a direct one-to-one relationship to periodic structures is not possible in the case of QC with non-crystallographic symmetry.

Furthermore, for both IMS and CS, the orientational (rotational point) symmetry does not place any constraint on the irrational length scales involved. This is different for QC, where, for instance, the number $\tau = 2 \cos \pi/5$ is related to 5-fold rotational symmetry.

Finally, we do not use the terms *quasicrystal* and *quasiperiodic structure* synonymously. QC may have strictly quasiperiodic structures with *non-crystallographic symmetry* in an idealized description. However, their structure may also be quasiperiodic on average only; or, even only somehow related to quasiperiodicity. Strictly quasiperiodic structures must obey the closeness condition in the nD description, this may not be the case for the structure of real QC, which then would correspond to a kind of lock-in state.

Structural Complexity

Unary phases A: If, due to only isotropic interactions, each atom is equally densely surrounded by the other atoms in the first coordination shell, dense sphere packings are the consequence. Atomic environment types (AET) can either be cuboctahedra, such as in *fcc cF*4-Al, or disheptahedra, such as in *hcp hP*2-Mg, with the coordination number CN=12 in both cases. In case of anisotropic interactions (directional bonding, magnetic interactions, disproportionation under pressure, etc.), more complex structures can form such as *cI*58-Mn or *oC*84-Cs-III.[4] Anisotropic interactions, however, can also lead to the geometrically simplest possible structure, that of *cP*1-Po.[5]

Binary phases A–B: In a binary intermetallic compound A_xB_y, each atom has to be surrounded by at least some atoms of the other species in order to maximize the number of attractive interactions, otherwise the pure element phases would separate. Stoichiometry, atomic size ratios, directionality of atomic interactions, and the electronic band structure determine the respective AET. These may comprise several coordination shells and are usually called clusters.

The size of the unit cell of an intermetallic compound is determined by the most efficient packing of its constituting AET (clusters), which is that with the lowest free energy, of course. Consequently, the most efficient packing can be quite different for high- and low-temperature phases due to the entropical contributions of thermal vibrations and chemical disorder. The complexity of binary intermetallic compounds ranges between *cP*2-NiAl and *mC*7,448-Yb_2Cu_9.[6]

Ternary phases A-B-C: On the one hand, three different constituents give more flexibility in optimizing interactions. On the other hand, particularly in the case of repulsive interactions between two of the three atom types, it can get much more difficult to realize the most efficient packing. More different AET or clusters may be needed to create the optimum environments of A, B, and C. The complexity of ternary intermetallic compounds ranges between *hP*3-BaPtSb[7] and *cF*23,158-$Al_{55.4}Cu_{5.4}Ta_{39.1}$.[8]

---

[4] McMahon, M.I., Nelmes, R.J., Rekhi, S.: Complex Crystal Structure of Cesium-III. Phys. Rev. Lett. **87**, art. no. 255502 (2001)

[5] Legut, D., Friák, M., Šob, M.: Why is polonium simple cubic and so highly anisotropic? Phys. Rev.Lett. **99**, art. no. 016402 (2007)

[6] Černý, R., François, M., Yvon, K., Jaccard, D., Walker, E., Petříček, V., Císařová, I., Nissen, H.-U., Wessicken, R.: A single-crystal x-ray and HRTEM study of the heavy-fermion compound $YbCu_{4.5}$. J. Condens. Matter **8**, 4485–4493 (1996)

[7] Villars, P., Calvert, L. D.: Pearsons Handbook of Crystallographic Data for Intermetallic Phases (ASM, USA), Vols. 1–4 (1991)

[8] Weber, T., Dshemuchadse, J., Kobas, M., Conrad, M., Harbrecht, B., Steurer, W.: Large, larger, largest - a family of cluster-based tantalum-copper-aluminides with giant unit cells. Part A: Structure solution and refinement. Acta Crystallogr. B **65**, 308–317 (2009)

In case of quasicrystals, the number of different clusters in a particular compound is small, usually only one or two. Quasiperiodic long-range order mainly originates from their non-crystallographic symmetry together with their ability to overlap in a well-defined way with each other.

The question is, how complex are quasicrystals compared to periodic intermetallics? Are they more complex than the most complex periodic compounds, such as cF23,158-$Al_{55.4}Cu_{5.4}Ta_{39.1}$, built from much more different unit clusters than any QC?

Structural complexity is difficult to define. It is certainly not sufficient to just count the number of atoms per unit cell, what would be impossible for a quasicrystal anyway. For instance, the 192 atoms located on the general Wyckoff position in a cubic unit cell with space group symmetry $Fm\bar{3}m$, can be described just by the coordinates of a single atom, i.e. 3 parameters. For the same number of atoms in a triclinic unit cell and space group $P1$, 576 parameters would be needed. On the other hand, it is also not just the number of free parameters. A cubic structure with space group symmetry $Fm\bar{3}m$ and 4 atoms per unit cell needs three parameters, as well, but it seems to be much simpler. Particularly, because it is just the cubic closest packing.

One possibility for indicating the degree of complexity could be the number of different AET or the R-atlas. The R-atlas of a structure consists of all different atomic configurations within a circle of radius R. This may work for comparing (quasi)periodic structures with (quasi)periodic ones, but not for comparing periodic with quasiperiodic structures. In the latter case, one could compare, for instance, the R-atlases up to a maximum R, which is given by the dimensions of the unit cell.

Another possibility would be to compare the information needed to fully describe the one and the other structure or to grow it in the computer.
Complexity is reflected in

- broad distribution functions (histogramms) of atomic distances,
- large number of different AETs for each kind of atom,
- large number of independent parameters for the description of a structure,
- low symmetry.

Complexity results from

- unfavorable size ratios of atoms hindering geometrically optimum interactions,
- preference of coordinations (AET, clusters) hindering optimum packings (e.g. 5-fold symmetry),
- parameters that are close to optimum but not optimal (pseudosymmetry).